



## Corrosion inhibition of steel by thiourea and cations under incomplete cathodic protection in a 3.5% NaCl solution and seawater

J.-C. LIN\*, S.-L. CHANG and S.-L. LEE

*Department of Mechanical Engineering, National Central University, Chung-Li, Taiwan 32054, Republic of China*  
(\*author for correspondence, e-mail: jclincom@rs250.ncu.edu.tw; fax: +886 3 4254501)

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### Abstract

This study investigates corrosion inhibition of steel using thiourea and cations such as aluminium, calcium and magnesium under cathodic control in a 3.5% NaCl solution and in seawater. Steel protection in a 3.5% NaCl solution is normally incomplete under a cathodic potential less electronegative than  $-1.100$  V. However, the protection can be enhanced by nearly 50% by adding either 50 ppm aluminium ion or 75 ppm thiourea in solution, and by almost 90% by the combined use of these additions. This study also analyzes how combining inhibitors and cathodic control may be used to protect steel. Moreover, this investigation monitors pH in the solution, measures zero-resistance current between the graphite-steel couple, as well as analyses cathode reaction products. A mechanism is also proposed to interpret the combined effects of inhibitors and cathodic control on the protection of steel.

### 1. Introduction

Corrosion of steel in a 3.5% NaCl aqueous solution can be inhibited either by the addition of cations and thiourea into the solution [1], or by cathodic control of the steel [2]. However, applying either approach alone intrinsically limits the inhibition. Adding cations and thiourea can cause some inhibitors to decompose, thus reducing inhibitive efficiency [3, 4], as the pH of the medium increases to a critical value. Also, some other inhibitors can lose their inhibitive properties, thereby accelerating corrosion at higher temperatures [1, 3, 4]. The cathodic control of steel is occasionally inefficient for a steel structure with a complicated geometry, or if the cathodic protection configuration is inadequately designed [5–8]. Controlling electrical potential is one of the major criteria for extending cathodic protection [2, 5]. The E–pH diagram demonstrates that steel can be completely protected at potentials more electronegative than  $-0.84$  V vs SCE in pure water at  $25^{\circ}\text{C}$ . However, this protection is incomplete in saline water unless the potential is equal to, or more electronegative than  $-1.100$  V vs SCE, due to the aggressive attack on steel by chloride ions [2, 5].

This study attempts to prevent steel corrosion by combining two techniques (inhibition and cathodic protection). Inhibitors such as cations and thiourea are added either alone, or together, to a 3.5% NaCl solution, in which steel is incompletely protected at potentials less electronegative than  $-1.100$  V vs SCE. The study then compared the effects of the inhibitors on the incompletely protected couple in a 3.5% NaCl solution and in seawater.

### 2. Experimental details

Cathodic protection of carbon steel was carried out in an electrolytic cell ( $10^{-3}$  m<sup>3</sup>) in which the steel acted as cathode and a dense graphite rod acted as the anode. The cathodic potential was controlled using a potentiostat (EG & G Parc-273) via a reference electrode, comprising a saturated calomel electrode (SCE) fitted with a Haber–Luggin probe. All potentials are reported against the SCE. A zero resistance ammeter was used to measure the current between the steel and the graphite. Preliminary tests revealed a drastic change in pH and current in 24 h, which levelled off subsequently. There-

fore, this work focused on the variations of pH and current with time during the initial 24 h.

Four sheets of low carbon steel of size 150 mm × 50 mm × 1 mm were used as the cathode. The chemical composition of the steel was (wt %): 0.04C:0.004Si:0.29Mn:0.011P:0.016S:bal.Fe. The steel was polished with a series of emery papers up to 600 mesh, degreased in acetone, and coated with epoxy resin on the upper portion to avoid water line corrosion. The four pieces of steel were connected through holes in their upper parts using a 2.5 mm diameter threaded copper rod. Copper rivets on the rod kept the pieces of steel 10 mm apart. The conducting rod and spaced rivets were coated with polytetrafluoroethylene (PTFE) to avoid galvanized corrosion with steel. A dense graphite rod, 8 mm in diameter, was used as the anode. The graphite was submerged in the corrosive medium, at a depth of 30 mm. Four pieces of the steel were placed symmetrically with respect to the graphite rod in the test solution. The total area of the steel specimen was 0.044 m<sup>2</sup> (0.011 m<sup>2</sup> × 4). The area ratio of steel to graphite was fixed at 150 to 1.

The inorganic salts and thiourea were of extra pure grade. Doubly distilled water was used to prepare the 3.5% NaCl solution and the synthetic seawater [9]. Cations (50 ppm) and thiourea (75 ppm) were added singly or together into the 3.5% NaCl solution to study the combined effect of inhibitors and cathodic protection. All experiments were performed under aeration to ensure a sufficient supply of dissolved oxygen. The corrosion products on the steel surface were removed using Clark's solution (ASTM test method G 1-72), and the corrosion rate (in  $\mu\text{g m}^{-2} \text{s}^{-1}$ ) was estimated from the weight loss (mg) of the steel at a fixed surface area and at a fixed immersion time (336 h). The data reported were obtained from triplicate experimental runs, with an accuracy of  $\pm 2\%$ . The precipitates on the steel surface derived from various cations, with and without cathodic polarisation, were dried at 95 °C, and were examined using an X-ray diffractometer (Shimadzu XD-5 XRD). Finally, the thiourea was analysed using an infrared spectrophotometer (Bio-Rad FTS-40 FTIR).

### 3. Results

#### 3.1. Effect of thiourea and cations on steel corrosion under incomplete cathodic protection

##### 3.1.1. Effect of thiourea

Figure 1 illustrates the corrosion rates for steel under cathodic protection in noninhibited (curve N) and inhibited (curve T) 3.5% NaCl solutions. In the nonin-

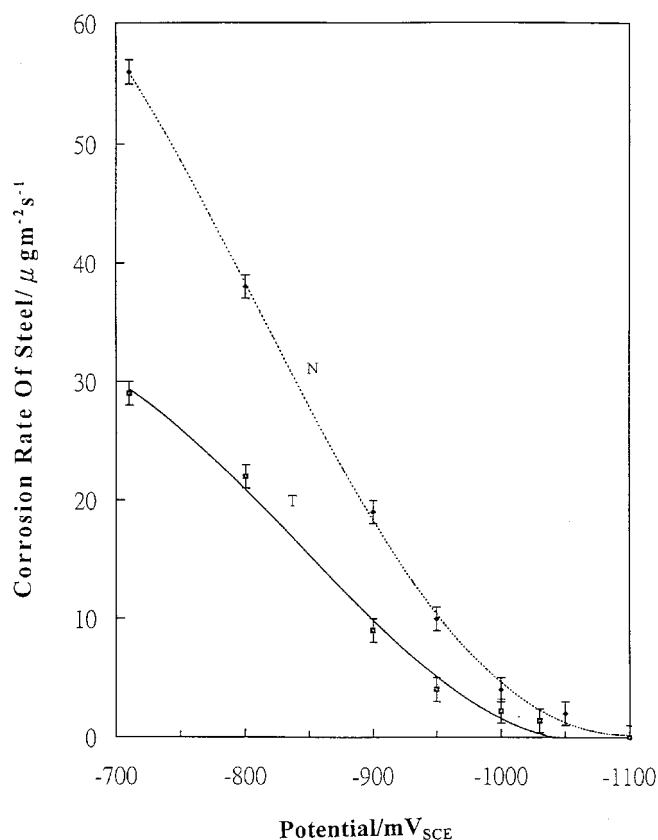


Fig. 1. Variation of corrosion rate for the steel with applied potential in a plain, 3.5% NaCl solution (N) and a 3.5% NaCl solution containing 75 ppm thiourea (T) in 336 h.

hibited solution, the corrosion rates of the steel at  $-0.84$  and  $-1.00$  V were 29 and  $2.9 \mu\text{g m}^{-2} \text{s}^{-1}$ , respectively. In the presence of thiourea, the corrosion rate of the steel was substantially lower than in the noninhibited system at corresponding cathodic potentials. The protection enhancement by thiourea was estimated quantitatively and was expressed as an inhibitive efficiency ( $\eta_{ie}$ ). This was calculated from a coupon test by the equation

$$\eta_{ie} = \frac{R_o - R_i}{R_o} \times 100 \quad (1)$$

where  $R_i$  and  $R_o$  are the corrosion rates of steel in inhibitive and noninhibitive solutions, respectively. As estimated from Figure 1,  $\eta_{ie}$  for thiourea is roughly 50% at potentials ranging from  $-0.700$  to  $-1.080$  V, and decreases immediately to 0% at potentials reaching  $-1.100$  V. Obviously, thiourea acts as an effective inhibitor when the cathodic protection of steel is incomplete. The contribution of thiourea becomes negligible as the steel is subjected to complete cathodic protection.

### 3.1.2. Effect of cations

As demonstrated in a related investigation [10], steel corrosion in a 3.5% NaCl solution is inhibited by adding certain cations, such as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Preliminary work in this study showed that, in the absence of cations, the steel cannot be protected completely at potentials less electronegative than  $-1.100\text{ V}$ . This investigation studied the role of cations at  $-0.94\text{ V}$ .

Table 1 summarizes the effect of some cations (50 ppm) on steel corrosion in a 3.5% NaCl solution and in seawater, at  $-0.94\text{ V}$ . The corrosion rate of steel in seawater at  $4.46\text{ }\mu\text{g m}^{-2}\text{ s}^{-1}$  was smaller than that in the 3.5% NaCl solution at  $8.60\text{ }\mu\text{g m}^{-2}\text{ s}^{-1}$ . The addition of cations in the 3.5% NaCl solution decreased steel corrosion. Among these cations,  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  were more inhibitive than  $\text{Mg}^{2+}$  (e.g.,  $\eta_{\text{ie}}$  51% > 46% > 19%). The variation in the inhibition is attributed to the different chemical behaviour of the cations and their corresponding precipitates. The chemistry of the cations in an aqueous solution is discussed later.

### 3.1.3. Combined effect of cations and thiourea

Table 2 presents the combined effects of cations and thiourea on steel corrosion at  $-0.94\text{ V}$ , in descending order according to the percentage inhibitive efficiency ( $\eta_{\text{ie}}$ ).  $\eta_{\text{ie}}$  for the S + A + T system (seawater containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea), the N + A + T system (3.5% NaCl solution containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea), the N + C + T system (3.5% NaCl solution containing 50 ppm  $\text{Ca}^{2+}$  and 75 ppm thiourea), the S + T system (seawater containing 75 ppm thiourea), the N + M + T system (3.5% NaCl solution containing 50 ppm  $\text{Mg}^{2+}$  and 75 ppm thiourea), and the N + T system (3.5% NaCl solution containing only 75 ppm thiourea) are 93%, 89%, 86%, 86%, 59% and 43%, respectively.

Table 1. Effect of cations on steel corrosion at  $-0.94\text{ V}$  in 336 h

Corrosion medium	Corrosion rate $/\mu\text{g m}^{-2}\text{ s}^{-1}$	Inhibitive efficiency, $\eta_{\text{ie}}$ /%
N	8.60	–
N + M	6.97	19
N + C	4.64	46
N + A	4.19	51
S	4.46	48
S + A	3.76	56

N: 3.5% NaCl solution S: seawater

N + M: 3.5% NaCl solution containing 50 ppm  $\text{Mg}^{2+}$

N + C: 3.5% NaCl solution containing 50 ppm  $\text{Ca}^{2+}$

N + A: 3.5% NaCl solution containing 50 ppm  $\text{Al}^{3+}$

S + A: seawater containing 50 ppm  $\text{Al}^{3+}$

Table 2. Combined effect of cations and thiourea on steel corrosion at  $-0.94\text{ V}$  in 336 h

Corrosion medium	Corrosion rate $/\mu\text{g m}^{-2}\text{ s}^{-1}$	Inhibitive efficiency, $\eta_{\text{ie}}$ /%
N	8.60	–
N + T	3.48	43
N + M + T	4.87	59
N + C + T	1.19	86
N + A + T	0.96	89
S + T	1.22	86
S + A + T	0.06	93

N: 3.5% NaCl solution

N + T: 3.5% NaCl solution containing 75 ppm thiourea

S + T: seawater containing 75 ppm thiourea

N + M + T: 3.5% NaCl solution containing 50 ppm  $\text{Mg}^{2+}$  and 75 ppm thiourea

N + C + T: 3.5% NaCl solution containing 50 ppm  $\text{Ca}^{2+}$  and 75 ppm thiourea

N + A + T: 3.5% NaCl solution containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea

S + A + T: seawater containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea

and 43%, respectively. In the systems where cations and thiourea are used together,  $\eta_{\text{ie}}$  is greater than in systems using a single addition. Obviously,  $\eta_{\text{ie}}$  depends on the kind of cations added, and whether thiourea is present. Preliminary tests have demonstrated that adding cations causes a pH change and that the extent of the change is determined by the kinds of cations added.

### 3.2. Variation of solution pH

Figure 2 displays the temporal variation of the pH in the 3.5% NaCl solution containing cations and thiourea, when the steel was controlled at  $-0.94\text{ V}$ . This study measured the pH curves for the systems containing cations alone (i.e., N + C, N + M, and N + A) and for those containing both cations and thiourea (i.e., N + C + T, N + M + T, and N + A + T). It was found that the pH was almost unchanged in the presence of thiourea. (For clarity, Figure 2 ignores the pH for the systems containing cations alone.) The initial pH values were 7.02, 6.90 and 6.70 for N, N + C + T, and N + M + T, respectively, and 4.85 for N + A + T. Systems N, N + C + T, and N + M + T exhibited an abrupt increase in pH (to 10.3, 10 and 8.5, respectively) after 4 h. The pH then decreased gradually in the alkaline region; the system N + A + T, however, revealed a steady decrease in pH in the acidic region (pH 4.85–4.50). This remarkable difference in pH profiles may be ascribed to competition between hydrolysis of the cations and electrode reactions, as detailed in the following discussion.

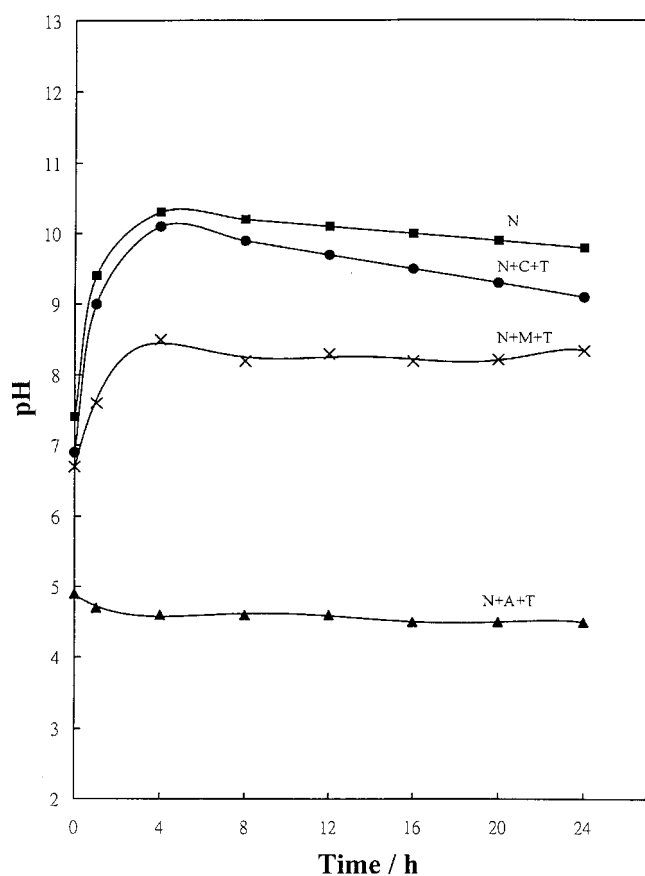


Fig. 2. Variation of solution pH with time, for steel at  $-0.94$  V. Key: (■) N: 3.5% NaCl solution; (●) N+C+T: 3.5% NaCl solution containing 50 ppm  $\text{Ca}^{2+}$  and 75 ppm thiourea; (x) N+M+T: 3.5% NaCl solution containing 50 ppm  $\text{Mg}^{2+}$  and 75 ppm thiourea; and (▲) N+A+T: 3.5% NaCl solution containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea.

### 3.3. Analysis of corrosion products

The investigation compared corrosion products on steel in the 3.5% NaCl solution containing 50 ppm cations, both with and without cathodic polarisation. Without cathodic polarisation, a longer immersion period (240 h) was needed to obtain a film with sufficient thickness for analysis. Some local sites on the steel surface were covered with brownish rust and all other portions were covered with whitish deposits. Upon removal of all the brownish rust, pitting corrosion was observed [11].

With cathodic polarization, a whitish film was rapidly produced in 24 h. Upon removal of the whitish film, no corrosion pits were observed. Evidently, cathodic control not only provided a cathodic current to protect the steel, but also accelerated the formation of hydroxide

ions that tend to form protective precipitates with cations.

In the absence of thiourea, amorphous hydroxides of aluminium and magnesium were formed in both N + A and N + M, whereas crystalline calcium carbonate was deposited in N + C. In the presence of thiourea, the magnesium hydroxide formed in N + M + T remained amorphous; however, a mixture of amorphous aluminium hydroxide and crystalline aluminium oxyhydroxide ( $\text{AlO}(\text{OH})$ ) was formed in N + A + T. This mixture had a compact structure. Figure 3 depicts the X-ray diffraction pattern of the film formed in N + A + T. The sharp peak corresponded to an increase in crystalline  $\text{AlO}(\text{OH})$  and the broad peak to an increase in amorphous aluminium hydroxide. The films formed in N + C and N + C + T were so thin that a longer duration (48 h) was required to accomplish the analysis. The precipitates formed in N + C and N + C + T were crystalline calcium carbonate.

### 3.4. Current between anode and cathode in 3.5% NaCl solution containing cations and thiourea

The current for the steel-graphite couple was measured in various solutions when the steel was controlled at  $-0.94$  V. As depicted in Figure 4, the current decreases abruptly after 4 h, and levels off in the subsequent 20 h. The current in the experiments using combined cations and thiourea was lower than in those using only cations. The current values were in the following order:  $\text{N} > \text{N} + \text{T} > \text{N} + \text{M} > \text{N} + \text{C} = \text{N} + \text{M} + \text{T} > \text{N} + \text{A} = \text{N} + \text{C} + \text{T} > \text{N} + \text{A} + \text{T}$ . (Two curves representing N + C and N + C + T are omitted in Figure 4 for clarity.)

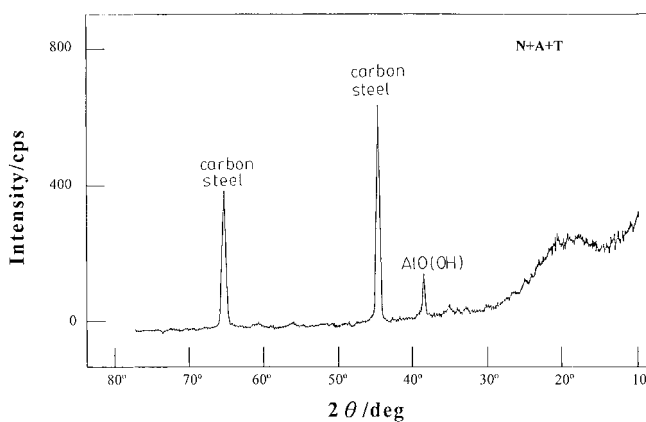


Fig. 3. X-ray diffraction pattern for the precipitate formed on steel in a 3.5% NaCl solution containing 50 ppm  $\text{Al}^{3+}$  and 50 ppm thiourea at  $-0.94$  V.

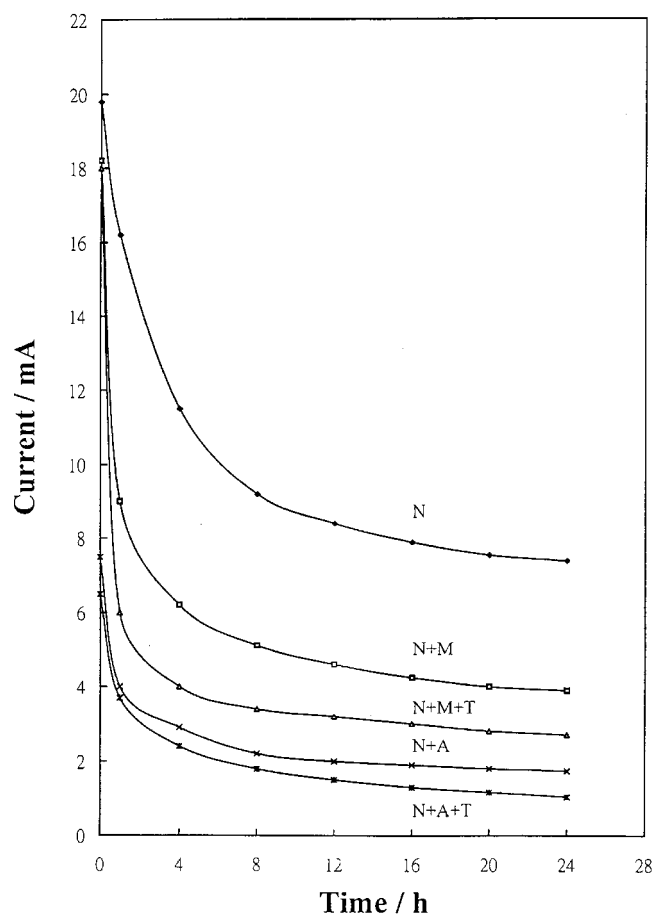


Fig. 4. Variation of current between steel and graphite with time, in various systems under a cathodic potential of  $-0.94$  V at  $20^\circ\text{C}$ . Key: ( $\blacklozenge$ ) N: 3.5% NaCl solution; ( $\square$ ) N+M: 3.5% NaCl solution containing 50 ppm  $\text{Mg}^{2+}$ ; ( $\triangle$ ) N+M+T: 3.5% NaCl solution containing 50 ppm  $\text{Mg}^{2+}$  and 75 ppm thiourea; ( $\times$ ) N+A: 3.5% NaCl solution containing 50 ppm  $\text{Al}^{3+}$ ; and ( $*$ ) N+A+T: 3.5% NaCl solution containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea.

### 3.5. Combined effect of thiourea and aluminium ion in artificial seawater

Figure 5 exhibits the single and combined effects of aluminium ion and thiourea on steel corrosion at  $-0.94$  V, in artificial seawater. Aluminium cations (50 ppm) were added singly (S + A) or in combination with 75 ppm thiourea (S + A + T). The composition (ppm) of the artificial seawater was 10560  $\text{Na}^+$ , 1270  $\text{Mg}^{2+}$ , 400  $\text{Ca}^{2+}$ , 380  $\text{K}^+$ , 18980  $\text{Cl}^-$ , 2650  $\text{SO}_4^{2-}$  and 142  $\text{HCO}_3^-$ . Apparently, magnesium and calcium cations were more concentrated in S + A and S + A + T than in N + M and N + C (i.e., 50 ppm). The precipitation was found more readily in the artificial seawater than in the 3.5% NaCl solution. This result is consistent with Yamaguchi's study [12].

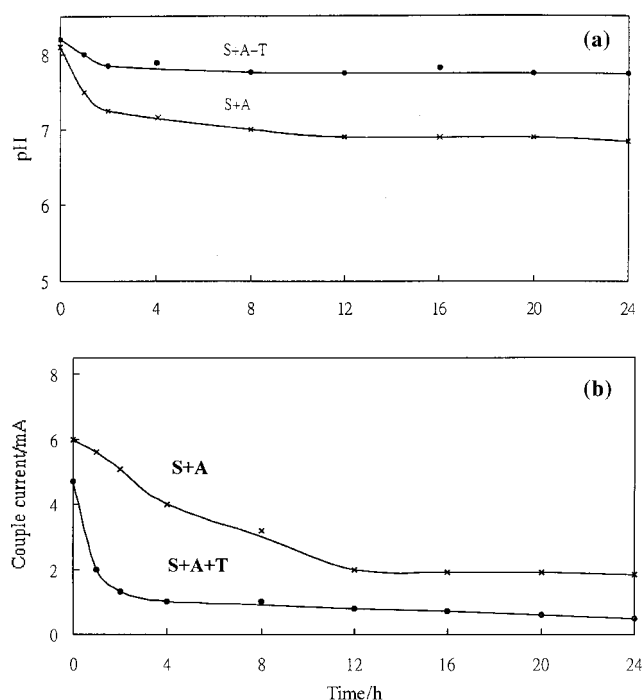


Fig. 5. (a) Variation of pH with time, in seawater containing aluminium ion without or with thiourea at  $20^\circ\text{C}$ . (b) Variations of the current between steel and graphite with time, in seawater containing aluminium ion without or with thiourea at  $20^\circ\text{C}$ . Key: ( $\times$ ) S + A: seawater containing 50 ppm  $\text{Al}^{3+}$  and ( $\bullet$ ) S + A + T: seawater containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea.

Figures 5(a) and (b), respectively, present pH and current as a function of time. Figure 5(a) demonstrates that the pH decreased in 4 h and then levelled off. The pH in S + A decreased quicker than the pH in S + A + T. Figure 5(b) demonstrates that the current in S + A decreased slower than the current in S + A + T. The variations of pH and current are detailed in later discussion.

Figure 6 exhibits the X-ray diffraction pattern for the precipitate formed in S + A + T. The precipitate comprised mainly crystalline calcium carbonate and aluminium oxyhydroxide.

## 4. Discussion

### 4.1. Corrosion inhibition of steel by thiourea under incomplete cathodic protection

This study indicated that the percentage inhibitive efficiency ( $\eta_{ie}$ ) for thiourea was roughly 50% for the steel that was controlled at potentials from  $-0.700$  to  $-1.080$  V. A previous study [1] indicated that it was only

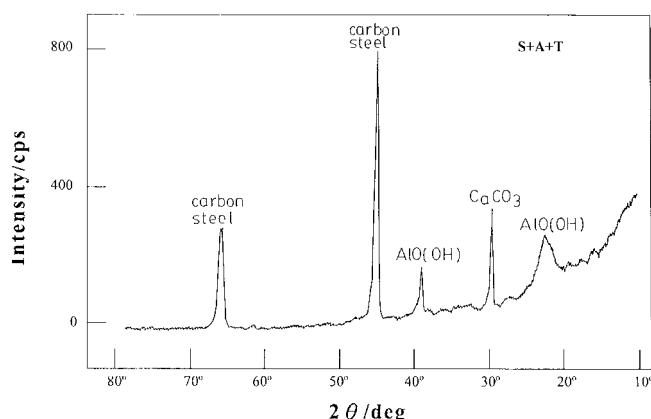


Fig. 6. X-ray diffraction pattern of the precipitate formed on steel in seawater containing 50 ppm  $\text{Al}^{3+}$  and 75 ppm thiourea at  $-0.94$  V.

13% in the absence of cathodic control. The increase in  $\eta_{ie}$  caused by applying cathodic control may be rationalized as follows. Thiourea ( $\text{H}_2\text{N}-(\text{C}=\text{S})-\text{NH}_2$ ) is a polar molecule in which the sulphur atom acts as an adsorption centre [13]. In the absence of an electric field, thiourea molecules are weakly adsorbed onto the steel through the interaction of the polar thiourea with the uncharged steel. In the presence of an electric field, the polar thiourea molecules are oriented and can be strongly adsorbed onto the negatively charged steel through the sulphur atom. Clearly, a stronger adsorption can result in an increase in the  $\eta_{ie}$ . At potentials beyond below  $-1.100$  V, the protection is complete by cathodic control alone, and so the contribution of thiourea is irrelevant.

The stability of thiourea in an electric field was also explored. A steel specimen, controlled at  $-0.94$  V in a 3.5% NaCl solution containing  $750 \text{ g m}^{-3}$  thiourea for 24 h, was examined using a reflectance infrared spectrophotometer. The infrared spectrum had the same patterns as that of pure thiourea. As well known, thiourea may decompose to foramidine disulphide and elemental sulphur. In this work, no peaks corresponding to formamidine disulphide and elemental sulphur were observed. It is believed that the thiourea is stable in the systems used.

#### 4.2. Precipitation on steel caused by cations

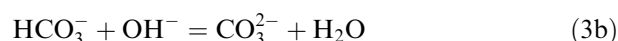
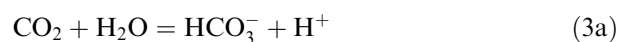
This study proposes a model to elucidate the inhibition mechanisms of steel corrosion in a 3.5% NaCl solution containing various cations under incomplete cathodic control. Cations (such as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ ) in aqueous solution are invariably enveloped with a water sheath, because of ion-dipole interaction between the

cations and water molecules [14]. This water sheath increases in size with increasing charge density of the cations. The charge density of a cation is defined as the ratio of its charge to its ionic radius. The ionic radius (nm) of the cations increases in the sequence [15]:  $\text{Al}^{3+}(0.051) < \text{Mg}^{2+}(0.066) < \text{Na}^+(0.095) < \text{Ca}^{2+}(0.099)$ . The smallest trivalent aluminium ion has the greatest charge density and has a large water sheath, whereas the monovalent sodium ion has the lowest charge density and has a smaller water sheath [14]. As for the divalent cations, calcium has a smaller water sheath than magnesium.

The hydrated cations may react with hydroxide or carbonate ions to form a precipitate on a steel surface under cathodic control [16]. The hydroxide ion is derived from the reduction of dissolved oxygen (through Equation 2(a)), or the reduction of water (through Equation 2(b)) on the steel surface [17]:



Dissolution of atmospheric carbon dioxide into water creates a minor source of carbonate ions in the 3.5% NaCl solutions as follows [17]:



In contrast, sodium bicarbonate provides a major source of carbonate ions in artificial seawater.

As mentioned earlier, the precipitates on the steel surface have different appearances. This difference may be ascribed to (i) a characteristic of the hydrated cations and (ii) the solubility of the precipitates.

The characteristic of the hydrated cations depends upon their charge densities. Raising the charge density of the cations enlarges the water sheath and increases the possibility of forming a diffused precipitate that adheres less well to the steel surface. This fact confirms that aluminium hydroxide is in a more diffused form than calcium carbonate [18].

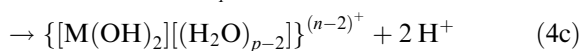
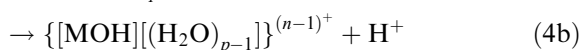
Cations react with certain anions to form a precipitate when their concentration product surpasses the solubility product ( $K_{sp}$ ) of this precipitate. The  $K_{sp}$  of some precipitates increases in the order  $\text{Al}(\text{OH})_3 (1.3 \times 10^{-33}) \ll \text{Mg}(\text{OH})_2 (1.8 \times 10^{-11}) < \text{CaCO}_3 (2.8 \times 10^{-9})$  [19]. A precipitate with a lower  $K_{sp}$  forms more readily than one with a higher  $K_{sp}$ , so the precipitation facility tends to decrease in the order  $\text{Al}(\text{OH})_3 \gg \text{Mg}(\text{OH})_2 > \text{CaCO}_3$ . This sequence implies that the coverage of precipitates on the steel has the order  $\text{N} + \text{A} \gg \text{N} + \text{M} > \text{N} + \text{C}$ .

According to related investigations, steel protection is controlled by the structure of a precipitate and the extent of its coverage on the steel [1, 11, 20–23]. Obviously, the greatest coverage exerted by aluminium hydroxide in the N + A system is the most protective. Although the coverage of precipitates formed in the N + M and N + C systems slightly differed, the structures of these precipitates markedly differed from each other. Calcium carbonate (formed in N + C) was in compact form, but magnesium hydroxide (formed in N + M) was in diffused form. A compact precipitate is denser than a diffused one, and thus is better at preventing the penetration of an aggressive ion. Hence, calcium carbonate is more protective than magnesium hydroxide. Considering both the coverage and the form of precipitates,  $\eta_{ie}$  decreases in the order N + A, N + C and N + M.

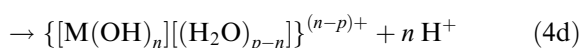
Measuring the current between graphite and steel (Figure 4) confirmed the results obtained from weight-loss tests. The electrical resistance of precipitates such as metal hydroxide and calcium carbonate is generally higher than the electrical resistance of steel. Steel covered with a heavy precipitate is more electrically resistant, so the current measured between the electrodes is lower. The greater the coverage of the precipitates implies a smaller current of the system. Hence, the current decreases in the order N > N + M > N + A. Figure 4 demonstrates that the magnitude of the current was in the following order: N + M + T < N + M and N + A + T < N + A. This result confirms that using a combination of thiourea and cations leads to the formation of a dense precipitate, thus providing superior protection [1, 12].

#### 4.3. Competition between hydrolysis of cations and electrode reactions

Competition between the hydrolysis of cations and the electrode reaction should be considered in the proposed model. The results in Figure 2 may be ascribed to indirect evidence of the competition. Prior to cathodic control, the pH in the solution was mainly governed by the hydrolysis of cations. The hydrolysis of a cation may be represented as [11]

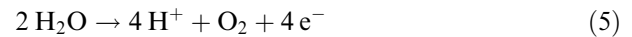


$\rightarrow \dots$



The cation with a higher charge density may hydrolyse more extensively. This releases more concentrated  $H^+$  to give a lower pH. According to the aforementioned order of charge density, the hydrolysis of cations increases in the order  $Na^+ < Ca^{2+} < Mg^{2+} < Al^{3+}$ . Thus, the initial pH (at  $t = 0$ ) in Figure 2 exhibits the order N > N + C > N + M > N + A.

When the steel is cathodically protected, the solution pH may be controlled not only by cationic hydrolysis but also by electrode reactions caused by the electric field. In the N, N + C systems, the hydrolysis of sodium and calcium is minor and can be ignored relative to the electrolysis of water that occurred on the electrodes. The solution pH is dominated by water electrolysis, in which water is oxidized on the graphite through Equation 5:



and is reduced simultaneously on the steel through Equation 2(b). Water is reduced to produce a huge amount of hydroxide ions on the steel. The hydroxide ions are diffused into the solution, causing pH to abruptly increase. The  $H^+$  produced on the graphite (Equation 5) then diffuses to the solution to neutralize the hydroxide ions. Consequently, the pH increases to reach a maximum then decreases steadily in the alkaline region.

The hydrolysis of aluminium cations is superior to water electrolysis in N + A and N + A + T systems. Hydroxide ion induced by water electrolysis causes only a little increase in pH (i.e., from 4.50 to 4.85). This change is then buffered by aluminium hydrolysis, thus returning the pH to 4.5. The inhibition in N + A + T is better than in N + A because thiourea is an effective inhibitor in acid solutions [1, 4, 23–25].

#### 4.4. Different behaviour in 3.5% NaCl and in artificial seawater

The precipitation form and its coverage on steel should be considered when comparing the cathodic protection of steel in artificial water and in 3.5% NaCl solutions containing 50 ppm single cations. In case the steel is controlled at the same cathodic potential, the concentrations of  $OH^-$  are kept at the same level in the two systems. However, the precipitate formed in the artificial seawater is much heavier than in the 3.5% NaCl solution, due to much greater concentrations of  $Mg^{2+}$ ,  $Ca^{2+}$  and  $CO_3^{2-}$  in the seawater. The precipitate formed in the S system was compact in structure and was named ‘calcareous film’ [26]; this precipitate adhered tightly onto the steel surface.

The inhibitive efficiency in S + A was greater than in S (Table 1). The precipitate formed in S + A was a mixture of calcium carbonate and aluminium hydroxide. This mixture gives greater coverage and is more protective than the calcareous film formed in S [27]. Both precipitates formed in S + A and in S are more compact and more protective than the simple  $\text{Al}(\text{OH})_3$  formed in N + A.

Thiourea plays an important role in the S + A + T. An adsorption of thiourea polarises the water electrolysis, thus decreasing the pH change in S + A + T compared with the pH change in S + A (Figure 5(a)). This polarization is also responsible for the smaller current found in S + A + T than in S + A, as displayed in Figure 5(b).

## 5. Conclusions

- (i) Cathodic protection of steel in a 3.5% NaCl solution is incomplete at an electrical potential less electronegative than  $-1.100\text{ V}$ . However, the protection is enhanced nearly 50% by the single addition of either 75 ppm thiourea or 50 ppm  $\text{Al}^{3+}$ , and roughly 90% through the combined use of both.
- (ii) The chemistry of hydrated cations determines the solution pH, controls the form of precipitates, and dominates the inhibition mechanism.

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